Stereochemistry of Iodine Addition to Acetylenes

Richard A. Hollins* and Marcos Pery A. Campos[1]

Instituto Militar de Engenharia, Praia Vermelha, Rio de Janeiro, RJ, Brasil

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We have studied the addition of iodine to a series of acetylenic substrates, including derivatives of propiolic acid, propyne, and phenylacetylene. Configurations of the resulting diiodoolefins were established, using ^1H and ^{13}C NMR analysis. In all cases, products of configuration *E* were obtained, and only with alkyl propiolates was there concomitant formation of the *Z* isomer. Additional evidence supporting the assignments for allylic products was obtained by the interconversion of these products. Application of a simple pairwise additivity of substituent shielding parameters allowed for a better agreement between calculated and observed ^{13}C chemical shifts for various products.

The addition of halogens to acetylenes has been little studied, with reports of iodine addition being particularly sparse despite its discovery and study almost a century ago.[2-6] Although most of the reports in this area have made claims as to the stereochemistry of products obtained, only a few recent works[7-10] do so based upon relatively unambiguous evidence. Research to date has also been very limited in scope, dealing primarily with iodine addition to derivatives of phenylacetylene or propiolic acid. In this paper, we present a more in depth study, both with regard to acetylenic substrate variety and stereochemical structure determination of products obtained.

Results and Discussion

Although several different methods are known for obtaining diiodoolefins, we have concentrated on the direct thermal, noncatalyzed addition of iodine to acetylenes. Reactions were usually effected by heating the acetylene with an excess of iodine in a suitable solvent. Workup by treatment with sodium metabisulfite to remove excess iodine followed by normal purification techniques in most cases led to quantitative yields of products. Table I presents a summary of our results.

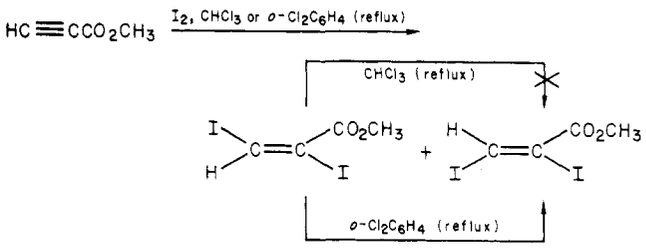
Configuration assignments are based principally on comparison of observed ^1H and ^{13}C NMR chemical shifts with calculated values derived using the additivity of individual substituent shielding increments Z_i.[11,12]

$$\delta_{calcd} = \text{base value} + \sum_i Z_i \qquad (1)$$

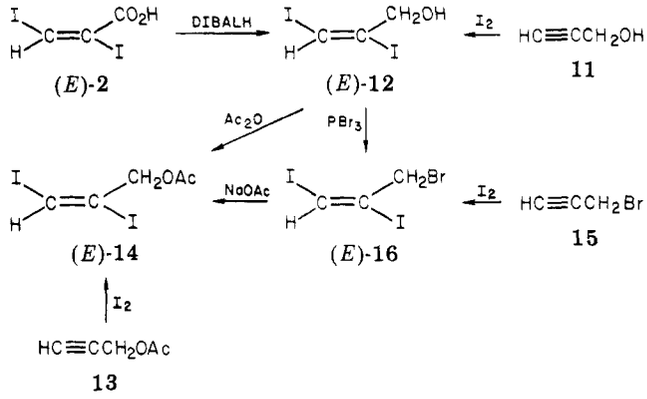
As will be shown later, we have also applied pairwise additivity to obtain better agreement with ^{13}C chemical shifts. Our results both confirm literature affirmations of stereochemistry for known compounds and provide reasonably conclusive assignments for new products presented herein.

Although both (*E*)- and (*Z*)-methyl 2,3-diiodoacrylates (**4** and **5**, respectively) are known,[7,13] only the former (*E*) is reported to result from the direct addition of iodine to methyl propiolate (**3**).[13] We have observed, however, the simultaneous formation of both isomers (Tables I and II) when the concentration of iodine is kept low by its slow addition to the acetylene **3**. Kai and Seki observed *E*–*Z* isomerization (resulting *E*–*Z* ratio of 5:3) when a sample of **4** was heated at its boiling point for 1 min, and the question was raised as to the possible formation of **5** in our reaction via subsequent thermal rearrangement of initially formed **4**. To test this possibility, we heated, at reflux, solutions of **4** and iodine in *o*-dichlorobenzene (20 h) and in chloroform (96 h). In *o*-dichlorobenzene, **4** was indeed observed to isomerize to the *Z* isomer (44%), and this could account for most of product **5** produced (48%) upon iodination of **3** in this solvent. After prolonged heating (96 h), this mixture reaches an equilibrium *E*–*Z* ratio of about 2:3. In chloroform, however, no interconversion occurred, and thus the *Z* isomer appears to be a primary product under these conditions (Scheme I). Ethyl propiolate also forms both *E* and *Z* products (Table I), whereas propiolic acid only led to (*E*)-2,3-diiodoacrylic acid (**2**) (Tables I and III), even at higher temperatures and low iodine concentrations.

Scheme I



Scheme II



Propargyl alcohol (**11**), acetate (**13**), and bromide (**15**) all lead to products of the same stereochemistry (**12**, **14**, and **16**, respectively), as evidenced by their interconversion (Scheme II). The assignment of configuration *E* was based

* Address correspondence to this author at 1033 Fairbrook Lane, Santa Ana, Calif. 92706.

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(4) J. V. Nef, *Justus Liebigs Ann. Chem.*, **308**, 323 (1899).
(5) P. Bruck, *Chem. Ber.*, **26**, 843(1893).
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(11) S. Matter, J. Pasqual, and P. Simon, *Tetrahedron*, **25**, 691 (1969).
(12) E. Lippmaa, T. Pehk, K. Andersson, and C. Rappe, *Org. Magn. Reson.*, **2**, 109 (1970).
(13) K. Ingold, *J. Chem. Soc.*, 1203 (1925).

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Table I. Iodination of Acetylenes

$$X\,C{\equiv}C\,Y \xrightarrow{I_2} IXC{=}CYI$$

	acetylene					
	X	Y	solvent	time, h[a]	product(s)	yield, %[b]
1	H	CO_2H	$CHCl_3$	20	(*E*)-2,3-diiodoacrilic acid (**2**)	100
3	H	CO_2CH_3	$CHCl_3$	20	methyl (*E*)-2,3-diiodoacrylate (**4**)	100
3	H	CO_2CH_3	$CHCl_3$[c]	96	methyl (*E*)-2,3-diiodoacrylate (**4**)	62
					methyl (*Z*)-2,3-diiodoacrylate (**5**)	38
3	H	CO_2CH_3	*o*-$Cl_2C_6H_4$[c]	20	methyl (*E*)-2,3-diiodoacrylate (**4**)	52
					methyl (*Z*)-2,3-diiodoacrylate (**5**)	48
6	H	$CO_2CH_2CH_3$	$CHCl_3$	96	ethyl (*E*)-2,3-diiodoacrylate (**7**)	87
					ethyl (*Z*)-2,3-diiodoacrylate (**8**)	13
9	CO_2CH_3	CO_2CH_3	*o*-$Cl_2C_6H_4$	20	dimethyl diiodofumarate (**10**)	100
11	H	CH_2OH	$CHCl_3$	5	(*E*)-α,β-diiodoallyl alcohol (**12**)	100
13	H	CH_2OAc	$CHCl_3$	10	(*E*)-α,β-diiodoallyl acetate (**14**)	100
15	H	CH_2Br	$CHCl_3$	48	(*E*)-α,β-diiodoallyl bromide (**16**)	100
17	H	C_6H_5	$CHCl_3$	10	(*E*)-α,β-diiodostyrene (**18**)	100
19	C_6H_5	$C{\equiv}CC_6H_5$	*o*-$Cl_2C_6H_4$	80	(*E*,*E*)-1,4-diphenyl-1,2,3,4-tetraiodobutadiene (**20**)[d]	62[e]

[a] All reactions were carried out at reflux. [b] Determined by ^1H NMR. [c] Slow addition of iodine; see text. [d] Tentative assignment; see text. [e] Isolated yield.

Table II. ^{13}C and ^1H Chemical Shifts of Methyl 2,3-Diiodoacrylates

$$HIC{=}CICO_2CH_3$$
$$\beta \quad \alpha$$

	δ $^{13}C_\alpha$[a]			δ $^{13}C_\beta$[a]			δ ^1H (vinyl protons)[a]	
compd	calcd[b]	calcd[c]	obsd	calcd[b]	calcd[c]	obsd	calcd[d]	obsd
(*E*)-**4**	95.0	85.8	85.55	83.0	86.5	87.34	7.75	7.72 (7.62)[e]
(*Z*)-**5**	104.0	102.9	110.04	87.0	103.6	112.18	8.45	9.05 (9.01)[e]

[a] Relative to Me_4Si (ppm). [b] By the method of Lippmaa et al. See ref 12. [c] Pairwise (I_2), using ^{13}C chemical shifts of $H_2C{=}CHCO_2CH_2CH_3$ for the base value. See ref 16. [d] See ref 11. [e] Chemical shifts observed for corresponding ethyl esters.

Table III. ^1H NMR Chemical Shifts of Substituted Diiodoethylenes

$$HIC{=}CIR$$

		δ ^1H (vinyl proton)[a]		
R		calcd[b]	obsd	Δδ[c]
CO_2H	"*E*"	7.91	8.05[d]	0.14
	"*Z*"	8.68	9.32[d]	0.64
CH_2OH	"*E*"	7.18	7.01	0.17
	"*Z*"	7.26		(0.25)
CH_2Br	"*E*"	7.16	7.09	0.07
	"*Z*"	7.38		(0.29)
CH_2OAc	"*E*"	7.18	7.10	0.08
	"*Z*"	7.26		(0.16)
C_6H_5	"*E*"	7.13	7.19	0.06
	"*Z*"	7.63		(0.44)

[a] Relative to Me_4Si (ppm). [b] See ref 11. [c] $[\delta_{calcd} - \delta_{obsd}]$; values in parentheses represent $[\delta_{calcd_Z} - \delta_{obsd_E}]$. [d] See ref 7.

upon comparison of their observed and calculated ^1H NMR chemical shifts[11] (Table III) and the reduction of (*E*)-2,3-diiodoacrylic acid (**2**) with diisobutylaluminum hydride (DIBALH) to (*E*)-α,β-diiodoallyl alcohol (**12**), identical with the product obtained from the iodination of propargyl alcohol.

Dimethyl acetylenedicarboxylate (**9**), when treated with iodine, gives in quantitative yield the same product (**10**) reported by Bruck in 1893.[5] We have confirmed Bruck's unsubstantiated assignments of **10** as the dimethyl diiodofumarate. The IR spectrum of **10** is strikingly similar to that of dimethyl fumarate and lacks absorption for the inactive C=C stretch as expected, but more convincing evidence was obtained from analysis of its ^{13}C NMR spectrum. Using the empirical technique of Lippmaa et al.[12,14] for calculating ^{13}C chemical shifts, we achieved qualitative agreement with the observed vinyl carbon shift. Applying the following justifiable[15] and intuitively more satisfying pairwise-substituent approach, however, we obtained considerably better agreement with the observed value:

Table IV. Vinyl ^{13}C Chemical Shifts[a] for Dimethyl Diiodofumarate

$$CH_3O_2CIC{=}CICO_2CH_3$$

config	calcd[b]	calcd[c]	obsd
E	96.7	88.5	90.51
Z	101.7	101.9	

[a] Relative to Me_4Si (ppm). [b] By method of Lippmaa et al. See ref 12. [c] Pairwise (I and CO_2CH_3) calculation; see text.

$$\delta[(Z)\text{-IHC=CHI (96.5 ppm)}] - \delta[H_2C{=}CH_2\ (123.3\ \text{ppm})] = -26.8\ \text{ppm} = Z_{((Z)\text{-I})} \quad (2)$$

$$\delta[(E)\text{-IHC=CHI (79.4 ppm)}] - \delta[H_2C{=}CH_2\ (123.3\ \text{ppm})] = -43.9\ \text{ppm} = Z_{((E)\text{-I})} \quad (3)$$

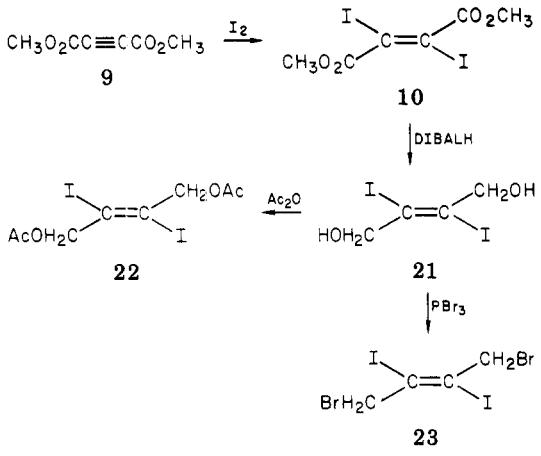
$$\delta[(Z)\text{-}CH_3O_2CHC{=}CHCO_2CH_3\ (128.7\ \text{ppm})] - \delta[H_2C{=}CH_2\ (123.3\ \text{ppm})] = +5.4\ \text{ppm} = Z_{((Z)\text{-}CO_2CH_3)} \quad (4)$$

$$\delta[(E)\text{-}CH_3O_2CHC{=}CHCO_2CH_3\ (132.4\ \text{ppm})] - \delta[H_2C{=}CH_2\ (123.3\ \text{ppm})] = +9.1\ \text{ppm} = Z_{((E)\text{-}CO_2CH_3)} \quad (5)$$

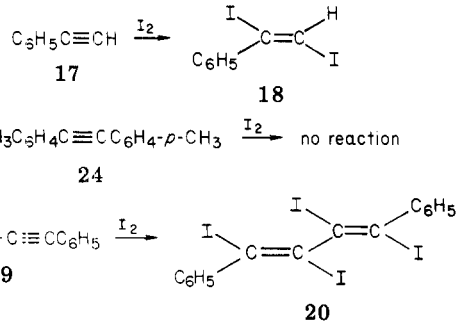
(14) We also included an additional deshielding factor of 2.1 ppm in accordance with the observed ^{13}C chemical shift differences between fumaric and maleic acids and their respective dimethyl esters. See ref 16.

(15) E. Malinowski, T. Vladimiroff, and R. Tavares, *J. Phys. Chem.*, 70, 2046 (1966).

Scheme III



Scheme IV



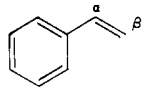
Again applying eq 1, where this time the base value is 123.3 ppm ($\delta[(H_2C{=}CH_2]$), and pairing $Z_{((Z)\text{-I}}$ with $Z_{((Z)\text{-}CO_2CH_3)}$ and $Z_{((E)\text{-I})}$ with $Z_{((E)\text{-}CO_2CH_3)}$, we obtained the values presented in Table IV. A similar treatment for the alkyl 2,3-diiodoacrylates also led to a better correlation between calculated and observed shifts (Table II).

Diester **10** is readily transformed into 1,4-disubstituted (*E*)-2,3-diiodobutenes, as shown in Scheme III. Retention of stereochemistry is assumed by analogy with the configurational stability observed in the reduction of **2** and the transformations of **12** and **16** (Scheme II).

Phenylacetylene (**17**) reacts quantitatively with iodine, giving (*E*)-α,β-diiodostyrene (**18**)[6] (Tables I and III), whereas di-*p*-tolylacetylene (**24**) proved to be totally unreactive, even at higher temperatures and prolonged reaction times. The failure of **24** to react probably results from steric factors, as it should be electronically similar to phenylacetylene but is lacking the unsubstituted terminus. Although considerably less reactive than phenylacetylene, diphenyldiacetylene (**19**) furnished 1,4-diphenyl-1,2,3,4-tetraiodobutadiene (**20**) (Scheme IV).

Both ^1H and ^{13}C NMR spectra indicate the equivalence of the two double bonds of **20**, and by simple analogy with the behavior of phenylacetylene one would tentatively assign the configuration *E,E*. Comparison of the ^{13}C NMR spectra of (*E*)-α,β-diiodostyrene (**18**) and **20** also leads us to conclude that the configuration of **20** is *E,E*. The ^{13}C chemical shifts (C_1, C_α, and C_β) for **18** are reasonable, considering the very large shielding effect on carbon directly substituted with iodine and a smaller deshielding effect for more remote carbon atoms.[16] In the butadiene derivative **20**, the presence of an additional double bond (relative to **18**) should lead to a small shielding of C_α and a large deshielding of C_β. The presence of iodine substituents in the additional double bond would deshield both carbons, especially C_β, for which the total extra deshielding in passing from structure **18** to (*E,E*)-**20** should be of the order of magnitude of +20 ppm, in accordance with the observed difference (Table V). If, on the other hand, **20** had configuration *Z,Z*, a further deshielding of up to 25 ppm might occur, as is noted in the case of the (*E*)- and (*Z*)-methyl-2,3-diiodoacrylates, and should lead to chemical shift values much larger than those actually observed.

Table V. ^{13}C Chemical Shifts of Styrenes



compd	δ $^{13}C_1$[a]	δ $^{13}C_\alpha$[a]	δ $^{13}C_\beta$[a]
styrene	137.3[b]	136.7[b]	113.2[b]
(*E*)-α,β-diiodostyrene	142.5	96.2	80.9
(*E,E*)-1,4-diphenyl-1,2,3,4-tetraiodobutadiene[b]	145.5	100.6[c]	105.3[c]

[a] Relative to Me_4Si (ppm). [b] See ref 19. [c] These assignments may be reversed.

In studying the halogenation of propiolic acid and derivatives, Berliner and Mauger[17,18] presented evidence for the intermediacy of cyclic or vinyl cations. In our work, however, reaction conditions and, in part, substrates are considerably different, and as such the same mechanism(s) may not be operative. In particular, we think it unlikely that dimethyl acetylenedicarboxylate would generate a localized vinyl cation intermediate, being, perhaps, a better candidate for iodonium ion formation or even nucleophilic attack.

Experimental Section

General. Melting points were taken on a Fischer-Johns melting-point apparatus and are uncorrected. Infrared spectra were obtained on Perkin-Elmer 180 and 135 spectrophotometers. ^1H NMR spectra were measured on a Hitachi Perkin-Elmer R 20B (60 MHz) spectrometer and are reported in parts per million downfield from internal tetramethylsilane. ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer. Mass spectra were recorded on a Varian Mat 111. Analyses were obtained, using a Perkin-Elmer 240 elemental analyzer.

General Procedure for Iodination of Acetylenes at a High Iodine Concentration. Method A. A solution of 0.05 mol of acetylenic substrate and 0.06 mol of iodine in 150 mL of chloroform or *o*-dichlorobenzene was heated at reflux with stirring until all starting acetylene was consumed, as is evidenced by ^1H NMR analysis. After cooling, the reaction mixture was washed with a 20% aqueous $Na_2S_2O_5$ solution and dried ($MgSO_4$), and the solvent was removed at reduce pressure.

General Procedure for Iodination of Acetylenes at a Low Iodine Concentration. Method B. To a stirred solution of 0.05 mol of acetylenic substrate in 150 mL of *o*-dichlorobenzene or chloroform at reflux were added 0.01-mol portions of iodine such that each portion reacted to completion (disappearance of iodine coloration) before subsequent additions were made. After completion of the reaction, as is evidenced by total consumption of starting acetylene (^1H NMR analysis), the mixture was cooled, washed with a 20% aqueous $Na_2S_2O_5$ solution, and dried ($MgSO_4$), and the solvent was removed at reduced pressure.

Methyl (*E*)-2,3-Diiodoacrylate (4). Prepared by method A (chloroform) in 100% yield, the product was recrystallized from methanol, giving pale yellow crystals: mp 37–38 °C (lit.[13] mp 37–38 °C); ^1H NMR ($CDCl_3$) δ 7.72 (s, 1, C=CH), 3.83 (s, 3, CH_3); ^{13}C NMR ($CDCl_3$) see Table II.

Methyl (*Z*)-2,3-Diodoacrylate (5). Preparation by method

(16) G. Levy and G. Nelson, "Carbon-13 Nuclear Magnetic Ressonance for Organic Chemists", Wiley-Interscience, New York, 1972.

(17) E. Berliner and E. Mauger, *J. Am. Chem. Soc.*, **94**, 194 (1972).
(18) E. Berliner and S. Ehrlich, *J. Am. Chem.Soc.*, **100**, 1525 (1978).
(19) K. S. Dhami and J. B. Stothers, *Can. J. Chem.*, **43**, 510 (1965).

B (chloroform gives a slightly lower percentage of isomer *Z* but is more easily removed than *o*-dichlorobenzene) gave a mixture of isomers *E* and *Z* (62:38) in 100% yield. An initial recrystallization from methanol caused the precipitation of the *E* isomer. The mother liquor, enriched in the *Z* isomer, was evaporated and recrystallized from heptane, producing crystals of both isomers which were separated with a spatula (low temperature) and furnishing a pure sample of **5**: mp 2–3 °C; ^{1}H NMR ($CDCl_3$) δ 9.05 (s, 1, C=CH) and 3.84 (s, 3, CH_3); ^{13}C NMR ($CDCl_3$) see Table II. Anal. Calcd for $C_4H_4I_2O_2$: C, 14.21; H, 1.18. Found: C, 14.38; H, 1.42.

Ethyl (*E*)- and (*Z*)-2,3-Diiodoacrylates (7 and 8). Mixtures of **7** and **8** were prepared by method B, using chloroform (Table I). The isomers were not separated, but C and H analyses were determined for the product mixture (liquid) obtained from the reaction in chloroform (^{1}H NMR indicated 13% *E*, 87% *Z*, and no impurities). Isomer (*E*)-**7**: ^{1}H NMR ($CDCl_3$) δ 7.62 (s, 1, C=CH), 4.28 (q, 2, CH_2, J = 7.5 Hz), and 1.35 (t, 3, CH_3, J = 7.5 Hz). Isomer (*Z*)-**8**: ^{1}H NMR ($CDCl_3$) δ 9.01 (s, 1, C=CH), 4.24 (q, 2, CH_2, J = 7.5 Hz), and 1.31 (t, 3, CH_3, J = 7.5 Hz). Anal. Calcd for $C_5H_6I_2O_2$: C, 17.04; H, 1.70. Found: C, 17.34; H, 1.80.

(*E*)-2,3-Diiodoacrylic Acid (2). Preparation using method A (chloroform) gave a 100% yield of colorless crystals: mp 103.5–105.5 °C (lit.[2] mp 104–106 °C); ^{1}H NMR ($CDCl_3$) δ 8.01 (s, 1, C=CH) and 10.4 (s, 1, OH). Anal. Calcd for $C_3H_2I_2O_2$: C, 11.13; H, 0.63. Found: C, 11.31; H, 0.66.

(*E*)-α,β-Diiodoallyl Alcohol (12). Obtained by method A (chloroform) in 100% yield, the product was recrystallized from hexane, furnishing colorless crystals: mp 53 °C; ^{1}H NMR ($CDCl_3$) δ 7.01 (s, 1, C=CH), 4.26 (s, 2, CH_2), and 2.69 (s, 1, OH). Anal. Calcd for $C_3H_4I_2O$: C, 11.61; H, 1.30. Found: C, 12.28; H, 1.45.

(*E*)-α,β-Diiodoallyl acetate (14) was obtained by method A (chloroform) in 100% yield as a pale yellow liquid (pure according to ^{1}H NMR analysis): n^{30}_D 1.6171; ^{1}H NMR ($CDCl_3$) δ 7.10 (s, 1, C=CH), 4.64 (s, 2, CH_2), and 2.05 (s, 3, CH_3). Anal. Calcd for $C_5H_6I_2O_2$: C, 17.04; H, 1.70. Found: C, 17.44; H, 1.81.

(*E*)-α,β-Diiodoallyl bromide (16) was obtained by method A (chloroform) in 100% yield as a pale yellow liquid (pure according to ^{1}H NMR analysis): n^{30}_D 1.3010; ^{1}H NMR ($CDCl_3$) δ 7.08 (s, 1, C=CH) and 4.28 (s, 2, CH_2). Anal. Calcd for $C_3H_3BrI_2$: C, 9.63; H, 1.09. Found: C, 9.69; H, 1.10.

Dimethyl diiodofumarate (10) was obtained by method A (*o*-dichlorobenzene) in 100% yield. After removal of solvent, the residue was dissolved in ethanol and the product precipitated with water. Recrystallization from methanol–water furnished colorless crystals: mp 125 °C (lit.[5] mp 126 °C); ^{1}H NMR ($CDCl_3$) δ 3.82 (s, 6, CH_3); ^{13}C NMR see Table IV; IR (KBr) 1725 (C=O) and 1252 cm^{-1}(C-O); mass spectrum *m/e* 396 (M^+, 50). Anal. Calcd for $C_6H_6I_2O_4$: C, 18.20; H, 1.53. Found: C, 18.30; H, 1.55.

(*E*)-α,β-Diiodostyrene (18). Obtained by method A (chloroform) in 100% yield, the product was recrystallized from methanol, furnishing colorless crystals: mp 76–77 °C (lit.[6] mp 76–77 °C); ^{1}H NMR ($CDCl_3$) δ 7.29 (s, 5, ArH) and 7.19 (s, 1, C=CH); ^{13}C NMR, see Table V; mass spectrum *m/e* 356 (M^+ 50). Anal. Calcd for $C_8H_6I_2$: C, 27.00; H, 1.70. Found: C, 27.37; H, 1.81.

(*E,E*)-1,2-Diphenyl-1,2,3,4-tetraiodobutadiene (20). The product was obtained by method A (*o*-dichlorobenzene; *o*-xylene was also used). After removal of solvent, the dark residue was recrystallized from methanol, giving a 62% yield of colorless crystals: mp 135–136 °C; ^{1}H NMR ($CDCl_3$) δ 7.34 (s, 10, ArH); ^{13}C NMR, see Table V. Anal. Calcd for $C_{16}H_{10}I_4$: C, 27.07; H, 1.42. Found: C, 27.08; H, 1.58.

DIBALH Reduction of (*E*)-2,3-Diiodoacrylic Acid (12). To 1 mL of a 20% benzene solution of DIBALH was added 0.9 g (2.8 mmol) of **2**, and the resulting solution was stirred for 3 h at room temperature. The mixture was then poured into 100 mL of 2-propanol containing 5 drops of water, filtered, and evaporated. The residue was extracted with chloroform, filtered, and evaporated to a solid. Recrystallization from methanol furnished 0.48 g (55%) of colorless crystals (mp 53 °C), identical in all aspects with **12** obtained from the iodination of propargyl alcohol.

Acetylation of 12 (14). A mixture of 0.31 g (1 mmol) of **12** and 0.11 g (1.1 mmol) of acetic anhydride in 8 mL of pyridine was stirred at room temperature for 3 h and then poured into 100 mL of ice water. The mixture was extracted with 50 mL of chloroform, and the extract was washed with 10% aqueous HCl (2 × 50 mL) then with water (2 × 50 mL) and dried ($MgSO_4$). Evaporation of the solvent at reduced pressure gave 0.32 g (90%) of a liquid identical in all aspects with **14**.

Reaction of 12 with PBr_3 (16). A mixture of 4.65 g (15 mmol) of **12** and 1.4 g (5.2 mmol) of PBr_3 in 50 mL of benzene was heated at reflux for 10 h. After cooling, the mixture was poured into 100 mL of ice water and rapidly extracted with 50 mL of chloroform. The extract was washed with cold 10% aqueous Na_2CO_3 (50 mL) and then with 50 mL of water and dried ($MgSO_4$). After filtration and evaporation of solvent, there was obtained 3.5 g (62%) of a pale yellow liquid identical in all aspects with **16**.

Reaction of 16 with NaOAc (14). A mixture of 0.37 g (1 mmol) of **16** and 0.09 g (1.2 mmol) of NaOAc in 10 mL of acetic acid was heated at reflux for 24 h. After being cooled, the mixture was poured into 100 mL of water and extracted with 50 mL of chloroform, and the extract was washed with 50 mL of 10% aqueous $NaHCO_3$ then 50 mL of water and dried ($MgSO_4$). After filtration and removal of solvent at reduced pressure, there was obtained 0.15 g (44%) of a liquid identical in all aspects with **14**.

(*E*)-2,3-Diiodo-2-butene-1,4-diol (21). A mixture of 7.9 g (20 mmol) of **10** in 10 mL of a 20% benzene solution of DIBALH was stirred at room temperature for 4 h and then poured into 500 mL of ethanol (99%). The mixture was filtered and evaporated, furnishing 3.0 g (44%) of colorless crystals: mp 175 °C; ^{1}H NMR (CD_3COCD_3/D_2O) δ 4.35 (s, 2, CH_2) and 3.65 (s, 1, OH). Anal. Calcd for $C_4H_6I_2O_2$: C, 14.14; H, 1.78. Found: C, 14.40; H, 1.84.

Acetylation of 21 (22). A mixture of 1.0 g (2.9 mmol) of **21** and 0.3 g (3 mmol) of acetic anhydride in 10 mL of pyridine was stirred at room temperature for 10 h and then poured into 100 mL of ice water. The mixture was extracted with 50 mL of chloroform, and the extract was washed with 10% aqueous HCl (2 × 50 mL) and then with water (2 × 50 mL) and dried ($MgSO_4$). The solvent was evaporated and the residue recrystallized from hexane, furnishing 0.36 g (28%) of colorless crystals: mp 65–67 °C; ^{1}H NMR ($CDCl_3$) δ 4.29 (s, 2, CH_2) and 3.10 (s, 3, CH_3). Anal. Calcd for $C_8H_{10}I_2O_4$: C, 22.64; H, 2.35. Found: C, 23.01; H, 2.39.

Reaction of 21 with PBr_3 (23). A mixture of 1.0 g (2.9 mmol) of **21** and 0.54 g (2.0 mmol) of PBr_3 in 50 mL of benzene was heated at reflux for 20 h. After being cooled, the mixture was poured into 100 mL of ice water and rapidly extracted with 50 mL of chloroform. The extract was washed with cold 10% aqueous Na_2CO_3 (50 mL) and then with 50 mL of water and dried ($MgSO_4$). After filtration and removal of solvent at reduced pressure, there were obtained 0.95 g (70%) of colorless crystals: mp 143 °C; ^{1}H NMR ($CDCl_3$) δ 4.48 (s, 2, CH_2). Anal. Calcd for $C_4H_4Br_2I_2$: C, 10.32; H, 0.87. Found: C, 10.50; H, 1.08.

Thermal Isomerization of 4. Solutions of 100 mg of **4** and 100 mg of iodine in 2 mL of chloroform or *o*-dichlorobenzene were heated at reflux and then analyzed by ^{1}H NMR spectroscopy. No isomerization occurred in chloroform (96 h). In *o*-dichlorobenzene, the mixture contained about 44% of the *Z* isomer after 20 h, and after 96 h equilibrium appeared to have been reached with an *E*–*Z* ratio of about 2:3.

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Registry No. **1**, 471-25-0; (*E*)-**2**, 14092-48-9; (*Z*)-**2**, 14173-06-9; **3**, 922-67-8; **4**, 71264-45-4; **5**, 14092-47-8; **6**, 623-47-2; **7**, 71264-46-5; **8**, 71264-47-6; **9**, 762-42-5; (*E*)-**10**, 18434-84-9; (*Z*)-**10**, 71264-48-7; **11**, 107-19-7; (*E*)-**12**, 71264-49-8; (*Z*)-**12**, 71264-50-1; **13**, 627-09-8; (*E*)-**14**, 71264-51-2; (*Z*)-**14**, 71264-52-3; **15**, 106-96-7; (*E*)-**16**, 71264-53-4; (*Z*)-**16**, 71264-54-5; **17**, 536-74-3; (*E*)-**18**, 71022-74-7; (*Z*)-**18**, 71264-55-6; **19**, 886-66-8; **20**, 71264-56-7; **21**, 62994-00-7; **22**, 71264-57-8; **23**, 71302-38-0; I_2, 7553-56-2; styrene, 100-42-5.